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2 pages of the Claims

12 pages of the Description

1 page of the drawing

[54] Title of the Invention

Preparation of maleic anhydride grafted ethylene- α -octylene copolymers

[57] The Abstract

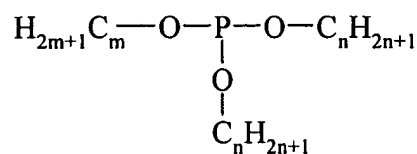
A graft copolymer of maleic anhydride and ethylene- α -octylene that is disclosed is prepared as follows: ethylene- α -octylene copolymer, maleic anhydride peroxide initiator and phosphite esters compounds are placed into a extruder or Banbury mixer to carry out melt grafting reaction to obtain maleic anhydride grafted ethylene- α -octylene copolymers. The maleic anhydride grafted ethylene- α -octylene copolymers prepared by said method is high in grafting rate and low in gel content. Said method provides a solution of how to strike a balance between grafting rate and gel contents in the field of maleic anhydride grafted polyolefin and overcomes the defects that the product is colored more or less, which has adverse influence on the application of the product.

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What is claimed:

1. A process for preparing maleic anhydride grafted ethylene- α -octylene copolymers, characterized in that the process comprises the steps of: feeding 100 parts by weight of ethylene- α -octylene copolymer, 0.05 to 15 parts by weight of maleic anhydride and 0.05 to 3 parts by weight of peroxide into an extruder or a Banbury mixer for melt grating reaction; feeding 0.02 to 5 parts by weight of phosphite esters compound into reaction system before gelation; mixing for another period of time, then discharging thus obtained material, wherein the reaction is carried out at a temperature between 130 and 170°C with a duration between 5 and 15 minutes.
2. A process according to claim 1, wherein by feeding phosphite esters compound into the reaction system before gelation it is meant that phosphite esters compounds are added at the time which is later than the other components by 1 to 3 minutes.
3. A process according to claim 1, wherein peroxides initiators are dicumyl peroxide or dibenzoyl peroxide.
4. A process according to claim 1, wherein phosphite esters compound is one selected from the group consisting of triphenyl phosphite, diphenyl alkyl phosphite, monophenyl dialkyl phosphite and trialkyl phosphite.
5. A process according to claim 4, wherein the monophenyl dialkyl phosphite is a compound having a formula of $(C_mH_{2m+1})(C_nH_{2n+1})(C_6H_5)PO_3$;
wherein $m=1$ to 10, $n=1$ to 10;
the diphenyl alkyl phosphite is a compound having a formula of $(C_nH_{2n+1})(C_6H_5)_2PO_3$,
wherein $n=1$ to 10;
the trialkyl phosphite is a compound having a formula of



wherein $m=1$ to 18, $n=1$ to 18, $n'=1$ to 18.

6. A process according to claim 1, characterized in that the melt grafting reaction is carried out in an extruder, ethylene- α -octylene copolymer, peroxide and maleic anhydride are pre-blended, and then the blend thus obtained is fed at a feed inlet in first stage, and phosphite esters compound is fed at a feed inlet in the second stage or the third stage of a feed cylinder, wherein the first stage has a temperature of between 130 and 135°C, the second stage between 150 and 170°C, and the third stage between 150 and 180°C, and a fourth stage between 170 and 190°C.

Process of Preparation of maleic anhydride grafted ethylene- α -octylene copolymers

Technical field

The present application relates to a process for preparing maleic anhydride grafted ethylene- α -octylene copolymers.

Background

Ethylene- α -octylene copolymer is a novel polyolefin thermal elastomer (POE) having a relatively narrow molecular weight distribution and a relatively narrow distribution of comonomer, and being controllable in structure, which is produced by **Dow Chemicals Corporation** of the United States by way of metallocene as a catalyst. This product has good mechanical performances and rheologic properties. Also, POE has a good affinity with polyolefin, a low temperature toughness and a high cost performance. Therefore, POE is widely used for toughening and modification of polyolefins. However, further application of POE is limited due to the fact that it is a non-polar polymer.

Maleic anhydride grafted polyolefin (PO) such as polyethylene (PE), polypropylene (PP) and ethylene-propylene rubber (EPR) can improve molecular polar of polyolefin and therefore are found a variety of applications. However, side reactions occur during the process of grafting of maleic anhydride onto polyolefin, such as breaking down of molecular chains, and crosslinking reaction among macromolecules. The content of gel in the product will increase with occurrence of crosslinking reaction, which leads to a significant increase in viscosity of processing system during processing of the product with deteriorating rheologic properties and difficult extrusion. It is the major problem in grafting maleic anhydride onto polyolefin, and another issue is how to increase grafting rate. Methods used in resolving the two problems include use of some auxiliaries to inhibit crosslinking reactions among macromolecules so as to lower the content of gel in the product while these auxiliaries also aid to facilitate main grafting reaction. Such auxiliaries include (1) monoolefin monomer, especially electron-rich monomers such as styrene, which is used for graft of maleic anhydride onto linear low density polyethylene (LLDPE) and polypropylene (PP) as described in US 4857254 assigned to Dupont, samay G, Nagy T, white J L. *J Appl Polym Sci*. 1995; 56:1423-1433, (2) electron-rich additives containing nitrogen (N), phosphors (P), sulfur (S) such as trinonylphenyl phosphite for use in graft of maleic anhydride onto linear low density polyethylene (LLDPE) system as described in N.G. Gaylord, *J Appl Polym Sci* 1992; 44:1041-1949. A scientific paper by HUANG Hua in *China Plastics*, 2000, 14 (12), 74-78) reported the use of stearamide in a process of preparing maleic anhydride grafted

ethylene- α -octylene copolymers. Use of these auxiliaries serves to inhibit to some degree the crosslinking reaction, but grafting rate of the product greatly lower simultaneously. The product thus obtained is more or less colored, which is not desirable in market.

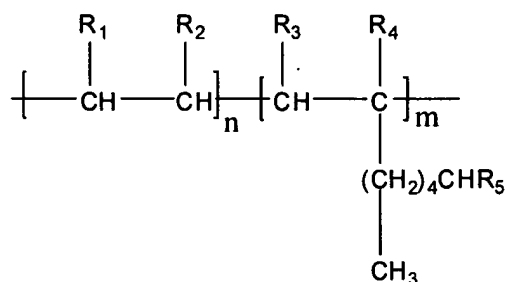
Polyethylene (PE), polypropylene (PP) and other olefin polymers have been widely used as materials. The corresponding maleic anhydride modified products have also been used in fields including fiberglass reinforced polyolefin, multilayer films for chemical and food packaging, and coating.

Therefore, development of a new process for preparation of maleic anhydride grafted modified POE will expect a bright future in various applications and commercial value.

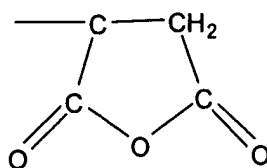
Summary of the invention

The object of the present invention is to provide a process for preparation of maleic anhydride grafted ethylene- α -octylene copolymers that can overcome the defects that the product has a low grafting rate and that the product is more or less colored. These defects may affect applications of the product.

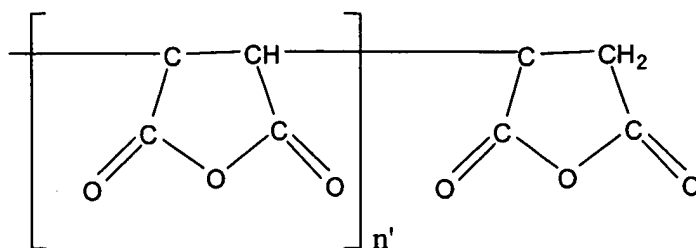
The maleic anhydride grafted ethylene- α -octylene copolymers of the present invention is a polymer having the following repeating nonstructural unit:



wherein: $n = 5000$ to 30000 , $m = 100$ to 3000
at least one of R_1 , R_2 , R_3 , R_4 and R_5 is



or



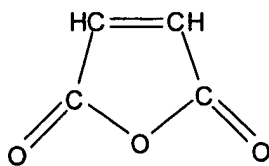
the remaining is H;
wherein: $n'=1$ to 5;

The above maleic anhydride grafted ethylene- α -octylene copolymer is prepared by the following steps:

Ethylene- α -octylene copolymers, maleic anhydrides (MAH), peroxides initiator and phosphite esters compounds are introduced into an extruder or a Banbury mixer to melt for grafting reaction. The obtained product is maleic anhydride grafted ethylene- α -octylene copolymer.

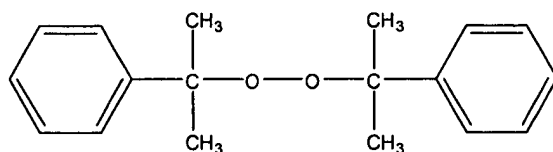
The ethylene- α -octylene copolymer is an ethylene-based elastomer copolymerized by ethylene and α -octylene. It is a novel polyolefin thermal elastomer (POE) successfully developed by **Dow Chemicals Corp** of the United States using metallocene as a catalyst. The polyolefin elastomer comprises 9.5 to 28% by weight of α -octylene, has a melt index (MFR, ASTM D-123B) of 1-30, a narrow relative molecular weight distribution and a narrow comonomer distribution.

The maleic anhydride which is an orthorhombic colorless crystal in needle or flake shape and is easy to ignite and sublime, has a melting point of 52°C, boiling point of 202°C, flashing point of 110°C, self-ignition point of 447°C, a relative density of 1.48 and it is dissolved in water to form maleic acid. At a temperature of 25°C, the solubility in a 100g solvent is 227g for acetone, 52.5g for chloroform, 50g for benzene, soluble in ethanol and generate ester, and that it is dissolved in ethanol to form ester. The maleic anhydride has a molecular formula of $C_4H_2O_3$, with a structural formula of:

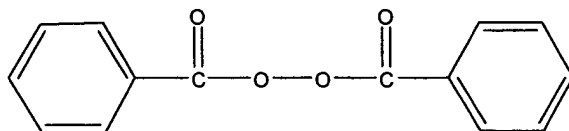


The peroxides initiators are dicumyl peroxide (DCP) or benzoyl peroxide (BPO).

The dicumyl peroxide is a colorless transparent crystal in diamond shape, which has a relative density of 1.082, melting point of 42°C, decomposing temperature of 120-125°C (rapid decomposing), sublime temperature of 100°C, flashing point of 133°C, self-ignition point of 218°C and is stable at room temperature. It is soluble in benzene, cumyl, ether, slightly soluble in ethanol and is not soluble in water. It has a molecular formula of $C_{18}H_{22}O_2$ with a structural formula of:

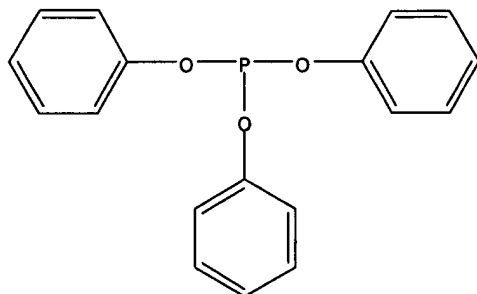


The benzoyl peroxide (BPO) is a white crystal powder having a melting point of 103-106°C. It is slightly soluble in water and ethanol, soluble in ether, acetone, chloroform and benzene and is flammable. It has a molecular formula of $(C_6H_5CO)_2O_2$ with a structural formula of:

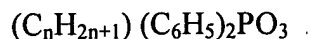


The phosphite esters compounds are triphenyl phosphite, diphenylalkyl phosphite, monophenyldialkyl phosphite and trialkyl phosphite.

The triphenyl phosphite is a colorless transparent liquid with slight bromophenol, is soluble in alcohol, benzene and acetone, and has a molecular formula of $C_{18}H_{15}O_3P$ with a structural formula of:

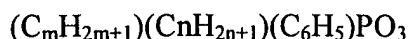


The diphenylalkyl phosphite has a general molecular formula: of



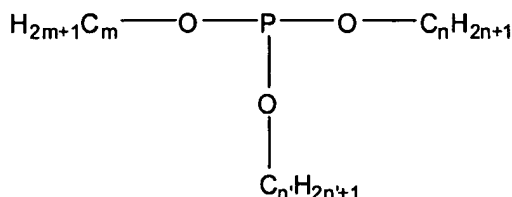
wherein: $n=1-10$

The monophenyldialkyl phosphite has a general molecular formula of:



wherein: $m=1-10$, $n=1-10$

The trialkyl phosphite has a general molecular formula of:



Wherein $m=1-18$, $n=1-18$, $n'=1-18$.

The components present in the maleic anhydride grafted ethylene- α -octylene copolymers in the following parts by weight:

ethylene- α -octylene copolymer	100 parts
maleic anhydride (MAH)	0.05-15 parts
peroxides initiators	0.05-3 parts
phosphite esters compounds	0.02-5 parts.

The phosphite esters compounds play an effective role in inhibiting gellation in the above formulations.

As grafting reaction and crosslinking reaction coexist in the process for preparing the maleic anhydride grafted ethylene- α -octylene copolymers, the content of gel in the product increases along with development of crosslinking reaction. However, polymer gelling occurs gradually and it has a critical value of gelling. Before reaching that value, the content of gel in the system does not increase although crosslinking reaction occurs, but the grafting rate increases continuously along with the progress of the reaction. Therefore, it is possible to obtain a product having high grafting rate and low gel content by adding an effective crosslinking inhibitor before arriving of the gelling critical value.

Therefore, a melt grafting process in which materials are fed in multiple steps is preferable:

(1) When using a Banbury mixer for grafting, changes of the materials in torque should be observed when ethylene- α -octylene copolymers, maleic anhydrides and

peroxides are at first pre-blended. Phosphite esters compounds are added to the reaction system before its arriving at the gelling critical value, then mixing for another period of time before the material is discharged.

(2) When using an extruder for melt grafting, ethylene- α -octylene copolymer, peroxide and maleic anhydride are firstly pre-blended. The blend thus obtained is fed from a charging open at the first stage and phosphite esters compounds are fed from a charging open at the second stage or the third stage of a feed cylinder.

The extruders used for the present invention are those having two or more than two charging opens. An extruder with three charging opens, Model SHL-35 twin-screw extruder is employed (*Shanghai No. 4 Chemical Mechanical Factory*).

The present invention uses ethylene- α -octylene as basic units and maleic anhydride as grafts to obtain a POE modified by maleic anhydride. The POE modified by maleic anhydride has a good interface adhesiveness with polar polymers, and good affinity with inorganic fillers and fiber-glass, which enlarges the application fields of POE. The phosphite esters compounds used in the present invention serve to function well in inhibiting crosslinking reaction and they also have a low volatility, which is advantageously in practice of production. In addition, addition of the phosphite esters compounds into the maleic anhydride grafted ethylene- α -octylene copolymers renders the grafts thus obtained colorless or light-colored. The process characterized by charging raw materials in multiple steps adopted in the present invention is simple and practical, which overcomes the disadvantages of low grafting rate as a result of formulations with auxiliary agents. Use of the phosphite esters compounds and the corresponding processing conditions can produce grafts with high grafting rate and low gel content, which provides a solution of how to strike a balance between grafting rate and gel content in the field of maleic anhydride grafted polyolefins.

Brief Description of The Drawings:

Fig 1 is a curve of system temperature as a function of torque of the materials in the Banbury mixer.

Embodiments of carrying out the invention:

The melt grafting reaction is carried out in a mixer:

Ethylene- α -octylene copolymer, maleic anhydride and peroxides initiators in a proportion are introduced into the mixing chamber of the Banbury mixer for blending for a period of time while the changing curve of torque is observed (Fig 1). The phosphite esters compounds are added into the mixing chamber of the Banbury mixer before peak of gel torque (point *a* appearing in Fig 1), and then the blending reaction

continues till the end of the set time to obtain the maleic anhydride grafted ethylene- α -octylene copolymers under the operation conditions of an initial reaction temperature of 130-170°C, rotation rate of 30-60 r/min and reaction time of 5-15 min.

The melt grafting reaction is carried out in an extruder:

Ethylene- α -octylene copolymer, maleic anhydride and peroxides initiators are preliminary-blended, and then feeding the blend from the charging open at the first stage of the extruder. The phosphite esters compounds are fed from the charging open at the second or third stage of the feed cylinder to obtain the maleic anhydride grafted ethylene- α -octylene copolymers with the operating parameters of a twin-screw extruder with diameter of 30 mm, length L to diameter D ratio of 28:1 and rotation rate of 160 r/min.

Temperature control:

First stage: 130-135°C, second stage: 150-170°C, third stage: 150-180°C, fourth stage: 170-190°C.

Measurement of properties:

(1) Determination of grafting rate of maleic anhydride

0.5g of the purified grafts is weighted precisely, and dissolving by heating with addition of 50 ml of xylene oil bath, then 10 ml KOH-ethanol solvent is added (titrated by standard oxalic acid-ethanol solution) to react for five minutes. After that reaction, it is retitrated with the oxalic acid-ethanol solution before cooling.

$$\text{rate of grafting} = \frac{M(V_2 - V_1) \times 98}{m} \times 100\%$$

wherein M: molar concentration of oxalic acid

V₂: the volume consumed of oxalic acid solution to titrate 10ml KOH-ethanol solution

V₁: the volume consumed of oxalic acid solution to titrate the grafts

m: the molar mass of the purified graft

(2) Measurement of gel content

The grafts are cut into pieces and put into a copper-web wrapper, then placing the copper-web wrapper into a Soxhlet extractor to be subjected to reflux and extraction for 6 hours by means of xylene. The copper-web wrapper is allowed to dry in an oven at a temperature of 80°C to constant mass after being taken out therefrom.

$$gel\ content = \frac{W_3 - W_1}{W_2 - W_1} \times 100\%$$

wherein:

W_1 is the mass of the copper-web and the packaging wire;

W_2 is the mass of the web wrapper with the sample;

W_3 is the mass of the web-wrapper after extraction.

The present invention is further described in detail with reference to the following examples, which however, cannot be considered to limit the present invention in any way at all.

Example 1

50g of ethylene- α -octylene copolymer, 0.75g of dicumyl peroxide (DCP) and 5g of maleic anhydride are pre-blended, then put into a Banbury mixer (Germany BRABENDER PL2100 torque rheometer). The initial temperature is set at 150°C, rotation rate is 60 r/min and reaction time is 10 minutes. The result is shown in Table 1.

Example 2

50g of ethylene- α -octylene copolymer, 0.75g of dicumyl peroxide (DCP), 5g of maleic anhydride and 1.5g of triphenyl phosphite are pre-blended, and then the homogeneously blended materials are added to a Banbury mixer (Germany BRABENDER PL2100 torque rheometer). The initial temperature is set at 150°C, rotation rate is 60 r/min and reaction time is 10 minutes. The result is shown in Table 1.

Comparative example 1

The experiment was repeated as set forth in example 2 except that the triphenyl phosphite is replaced by the triphenyl phosphate. The result is shown in Table 1.

Example 3

50g of ethylene- α -octylene copolymer, 0.75g of dicumyl peroxide (DCP), 5g of maleic anhydride and 1.5g of diphenyl decyl phosphite are pre-blended, then the homogeneously blended materials are added to a Banbury mixer (Germany BRABENDER PL2100 torque rheometer). The initial temperature is set at 150°C, rotation rate is 60 r/min and period of time for reaction is 10 minutes. The result is shown in Table 1.

Example 4

50g of ethylene- α -octylene copolymer, 0.75g of dicumyl peroxide (DCP), 5g of maleic anhydride and 1.5g of phenyl didecyl phosphite are pre-blended, the homogeneously blended materials are then added to a Banbury mixer (Germany BRABENDER PL2100 torque rheometer). The initial temperature is set at 150°C, rotation rate is 60 r/min and reaction time is 10 minutes. The result is shown in Table 1.

Example 5

50g of ethylene- α -octylene copolymer, 0.75g of dicumyl peroxide (DCP), 5g of maleic anhydride and 1.5g of tridecyl phosphite are pre-blended, the homogeneously blended materials are then added to a banbury mixer (Germany BRABENDER PL2100 torque rheometer). The initial temperature is set at 150°C, rotation rate is 60 r/min and period of time for reaction is 10 minutes. The result is shown in Table 1.

Table 1

Samples	Grafting rate %	Gel Content %
Example 1	2.07	73.41
Example 2	0.9	0.45
Comparative Example 1	1.98	72.45
Example 3	0.92	5.62
Example 4	0.85	7.44
Example 5	0.94	4.63

It can be seen from examples 1 and 2 that the gel content has been reduced to almost 0 after addition of triphenyl phosphite, which demonstrates that triphenyl phosphite plays a role in gel inhibiting in the maleic anhydride grafted ethylene- α -octylene copolymers. It also can be seen from example 2 and comparative example 1 that triphenyl phosphate does not show the corresponding effects of gel inhibiting. It can be seen from examples 2, 3, 4 and 5 that all of the triphenyl phosphite, diphenyl decyl phosphite, phenyl didecyl phosphite and tridecyl phosphite show gel inhibiting to some degrees with triphenyl phosphite being more effective.

Example 6

50g of ethylene- α -octylene copolymer, 0.75g of benzoyl peroxide (BPO), 5g of maleic anhydride and 1.5g of triphenyl phosphite are pre-blended, and the homogeneously blended materials are added to a Banbury mixer (Germany BRABENDER PL2100 torque rheometer). The initial temperature is set at 150°C, rotation rate is 60 r/min and the period of time for reaction is 10 minutes. The result

is shown in Table 2.

Table 2

Samples	Grafting rate %	Content of gel %
Example 2	0.9	0.45
Example 6	0.95	0.54

It can be seen from Table 2 that use of dicumyl peroxide (DCP) or benzoyl peroxide (BPO) as an initiator has almost the same effects.

Example 7

50g of ethylene- α -octylene copolymer, 0.75g of dicumyl peroxide (DCP), 5g of maleic anhydride are pre-blended, and the homogeneously blended materials are added to a Banbury mixer (Germany BRABENDER PL2100 torque rheometer) for reaction for a period of time. 1.5g of triphenyl phosphite is added to the reaction system at the second minute and the reaction continues till the end of the set time. The initial temperature is set at 150°C, rotation rate is 60 r/min and reaction time is 10 minutes. The result is shown in Table 3.

Example 8

50g of ethylene- α -octylene copolymer, 0.75g of dicumyl peroxide (DCP), 5g of maleic anhydride are pre-blended, the homogeneously blended materials are then added to a Banbury mixer (Germany BRABENDER PL2100 torque rheometer) for reaction for a period of time. 1.5g of triphenyl phosphite is added to the reaction system 1 minute and 40 seconds later after the reaction starts and the reaction continues till the end of the set reaction time. The initial temperature is set at 150°C, rotation rate is 60 r/min and the period of time for reaction is 10 minutes. The result is shown in Table 3.

Example 9

50g of ethylene- α -octylene copolymer, 0.75g of dicumyl peroxide (DCP), 5g of maleic anhydride are pre-blended, the homogeneously blended materials are then added to a Banbury mixer (Germany BRABENDER PL2100 torque rheometer) for reaction for a period of time. 1.5g of triphenyl phosphite is added to the reaction system 1 minute and 10 seconds later after the reaction starts and the reaction continues till the end of the set reaction time. The initial temperature is set at 150°C, rotation rate is 60 r/min and the periods of time for reaction is 10 minutes. The result is shown in Table 3.

Table 3

Samples	Grafting rate%	Gel Content %
Example 7	1.95	10.5
Example 8	1.56	1.84
Example 9	1.10	0.64
Example 2	0.92	0.45

It can be seen from Table 3 that different grafts can be obtained by adding the triphenyl phosphite at different times. In the present invention, the graft with high grafting rate and low gel content is obtained by controlling the time when the triphenyl phosphite is added, as shown in example 7.

Example 10

50g of ethylene- α -octylene copolymer, 0.75g of benzoyl peroxide (BPO) and 5g of maleic anhydride are pre-blended, the homogeneously blended materials are then added to a Banbury mixer (Germany BRABENDER PL2100 torque rheometer) for reaction for a period of time. 1.5g of triphenyl phosphite is added to the reaction system at the second minute after the reaction starts and the reaction continues till the end of the set reaction time. The initial temperature is set at 150°C, rotation rate is 60 r/min and reaction time is 10 minutes. The result is shown in Table 4.

Example 11

50g of ethylene- α -octylene copolymer, 0.75g of benzoyl peroxide (BPO) and 5g of maleic anhydride are pre-blended, the homogeneously blended materials are then added to a Banbury mixer (Germany BRABENDER PL2100 torque rheometer) for reaction for a period of time. 1.5g of triphenyl phosphite is added to the reaction system one minute and 40 second later after the reaction begins and the reaction continues till the end of the set reaction time. The initial temperature is set at 150°C, rotation rate is 60 r/min and reaction time is 10 minutes. The result is shown in Table 4.

Example 12

50g of ethylene- α -octylene copolymer, 0.75g of benzoyl peroxide (BPO) and 5g of maleic anhydride are pre-blended, the homogeneously blended materials are then added to a Banbury mixer (Germany BRABENDER PL2100 torque rheometer) for reaction for a period of time. 1.5g of triphenyl phosphite is added to the reaction system one minute and 10 second later after the reaction starts and the reaction continues till the end of the set reaction time. The initial temperature is set at 150°C, rotation rate is 60 r/min and reaction time is 10 minutes. The result is shown in Table 4.

Table 4

Samples	Grafting rate%	Gel Content %
Example 10	1.90	9.56
Example 11	1.46	2.84
Example 12	1.0	1.64

It can be seen from Table 4 that use of benzoyl peroxide (BPO) as an initiator has the testing results very close to that with use of dicumyl peroxide (DCP) as an initiator.

Example 13

100 parts of ethylene- α -octylene copolymer, 10 parts of maleic anhydride, 1.5 parts of dicumyl peroxide (DCP) are pre-blended. The blend is then fed from the charging open of the extruder. The triphenyl phosphite is fed from the charging open at the second stage of the feed cylinder. Operating parameters are as follow: a twin-screw extruder with diameter of 30 mm, L/D ratio of 28:1 and rotation rate of 160 r/min.

Temperature control:

First stage: 135°C, second stage: 170°C, third stage: 175°C, fourth stage: 170°C. The result is shown in Table 5.

Example 14

100 parts of ethylene- α -octylene copolymer, 10 parts of maleic anhydride, 1.5 parts of benzoyl peroxide (BPO) are pre-blended. The blend is fed from the charging open of the extruder. The triphenyl phosphite is fed from the charging open at the second stage of the feed cylinder. Operating parameters are as follow: a twin-screw extruder with diameter of 30 mm, L/D ratio of 28:1 and rotation rate of 160 r/min.

Temperature control:

First stage: 135°C, second stage: 170°C, third stage: 175°C, fourth stage: 170°C. The result is shown in Table 5.

Table 5

Samples	Grafting rate%	Gel Content %
Example 13	2.35	8.65
Example 14	2.21	9.31

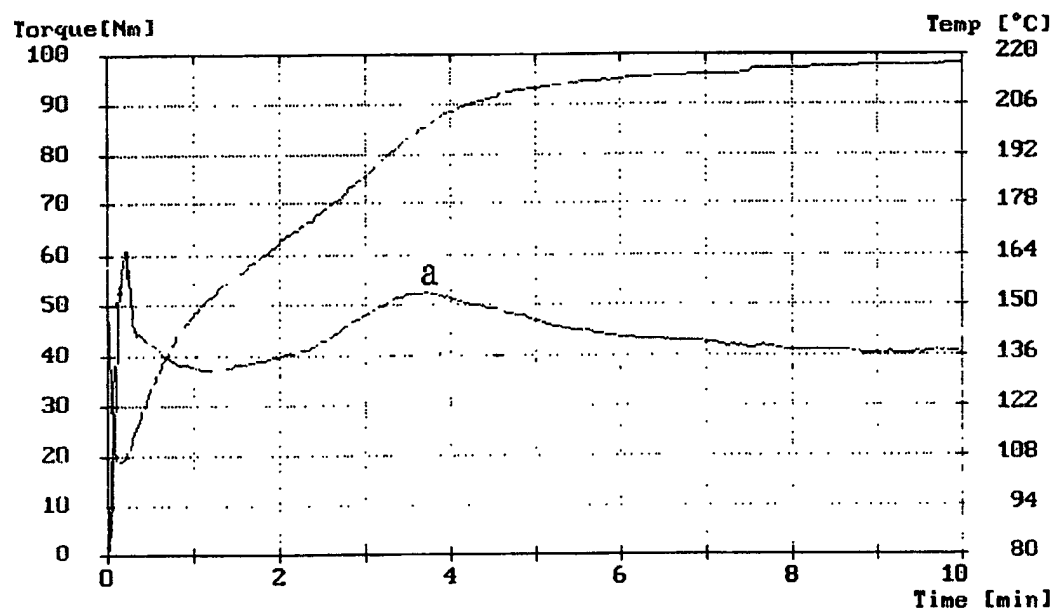


Fig 1